Problem 8: Phonon dispersions and thermodynamic properties of Tl - PBE pseudopotential

In this exercise we study ab-initio the phonon dispersions of tallium. Tallium is an hcp crystal with two atoms in the unit cell. The experimental lattice parameters are $a = 3.46$ Å and $c = 5.53$ Å. We compute the total energy of tallium using density functional theory. You can use the pseudopotential `Tl.pbe-dn-kjpaw_psl.1.0.0.UPF` from `pslibrary` for the PBE functional.

1. At the experimental structure, study the convergence of the total energy as a function of the kinetic energy cut-off of the wavefunctions and determine for which value the energy is converged within 1 mRy. Keep the charge density cut-off equal to 4, 6, or 8 times the cut-off for the wavefunctions. Discuss how the results change. For this calculation use a smearing parameter 0.02 Ry and a **k**-point mesh equal to $(12, 12, 8)$.

2. At the cut-offs determined at the previous point, study the convergence of the energy with the **k**-point sampling. Repeat the calculation for smearing parameters 0.02 Ry, 0.01 Ry, and 0.005 Ry. Discuss the convergence of the results and, if necessary, decrease or increase further the smearing.

3. Using the option `calculation='vc-relax'` in the `pw.x` input determine the equilibrium values of a and c/a at zero pressure. Discuss their convergence with the kinetic energy cut-offs and **k**-point sampling.

4. At the equilibrium values of a and c/a determine the phonon frequencies at the point Γ, K, M, A, H and L of the Brillouin zone. Study their convergence with the kinetic energy cut-offs and **k**-point sampling.

5. Using the parameters for which previous frequencies are converged within 3 cm^{-1} plot the complete phonon dispersions of tallium comparing with the experimental data mentioned in S. S. Kushwaha and J. S. Rajput, J. Phys. F: Met. Phys. **1**, 377 (1971).

6. (optional) Compute the phonon frequencies on a thick mesh of **q** points and calculate the phonon density of states of tallium. Use the phonon density of states to calculate the vibrational contribution to the free energy, to the entropy and to the isochoric heat capacity.